

# Crystal field and related phenomena in hexagonal close-packed H<sub>2</sub> and D<sub>2</sub> under pressure

Yu. A. Freiman,<sup>1,\*</sup> S. M. Tretyak,<sup>1</sup> Alexei Grechnev,<sup>1</sup> Alexander F. Goncharov,<sup>2,3</sup> and Russell J. Hemley<sup>2</sup>

<sup>1</sup>*B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine, 47 Lenin avenue, Kharkov, 61103, Ukraine*

<sup>2</sup>*Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington, DC 20015, USA*

<sup>3</sup>*Center for Energy Matter in Extreme Environments and Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, 350 Shushanghu Road, Hefei, Anhui 230031, China*

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The lattice distortion parameter (the deviation of the  $c/a$  ratio from the ideal value 1.633), orientational order parameter, and crystal-field parameter in hexagonal close-packed (hcp) lattice of  $p$ -H<sub>2</sub>,  $o$ -D<sub>2</sub> and  $n$ -H<sub>2</sub> are calculated using the semi-empirical lattice-dynamic approach. It is shown that the lattice distortion in the  $J$ -even species is two order of magnitude smaller compared with that found in  $n$ -H<sub>2</sub>, and  $n$ -D<sub>2</sub>. The difference is due to the splitting of the  $J$ -odd rotational levels in the  $J$ -even -  $J$ -odd mixtures.

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At zero pressure and temperature the molecules in  $J$ -even ( $p$ -H<sub>2</sub>,  $o$ -D<sub>2</sub>) and  $J$ -all (HD) solid hydrogens are in the ground state  $J = 0$ . Admixtures of higher rotational states into the ground-state wave function are very small and the molecules are virtually spherical. Rigid spheres crystallize into the face center cubic (fcc) or hexagonal close-packed (hcp) lattices. As compared with fcc, hcp lattice has an additional degree of freedom associated with the axial  $c/a$  ratio. The lattice of close-packed hard spheres has  $c/a = \sqrt{8/3} \approx 1.633$  (an ideal hcp structure). The quantity  $\delta = c/a - \sqrt{8/3}$ , the lattice distortion parameter, describes the deviation of the axial ratio from the ideal value. In the case of  $\delta < 0$ , this distortion involves an expansion within close-packed planes, and contraction along the  $c$ -axis direction, and vice versa, for  $\delta > 0$  the lattice is expanded along the  $c$ -axis and contracted within the close-packed planes.

Calculations with simple isotropic pair potentials have shown that the ideal hcp lattice at zero pressure and temperature does not minimize the lattice energy [1–3], and the hcp lattice with the minimal energy has a small but nonzero lattice distortion. Semi-empirical and DFT calculations performed for solid He and hcp rare-gas solids (RGS) showed [4, 5] that the pressure dependencies of the lattice distortion parameter  $\delta$  for the many-body (two- plus three-body) and

for the pair intermolecular potentials are qualitatively different. The three-body forces flatten the lattice ( $\delta < 0$ ) while the pair forces at large compressions tend to elongate it ( $\delta > 0$ ). Thus it was shown that the lattice distortion parameter is a thermodynamic quantity, which is very sensitive to the many-body component of the intermolecular potential and can therefore be used as a probe of the many-body forces [6].

The deviation of the axial ratio from the ideal value can be attributed ultimately to a lowering of the band-structure energy through lattice distortion. In the case of solid hydrogens the effect of lattice distortion both on the isotropic and rotational components of the ground-state energy is essential.

For all hcp elemental solids except helium, hydrogen, and high-pressure Ar, Kr, and Xe the behavior of  $\delta$  with pressure and temperature is well established from both theory and experiment. Typical values are of the order of  $10^{-2}$  [7]. For solid helium  $\delta$  is one-two orders of magnitude smaller [4, 5]. The first measurements of  $c/a$  ratio in solid hydrogens were done by Keesom *et al.* [8], who found that at zero pressure the hcp lattice of  $p$ -H<sub>2</sub> is close to the ideal one. X-ray zero-pressure study by Krupskii *et al.* [9] confirmed this result ( $c/a = 1.633 \pm 0.001$ ) and extended it to the  $o$ -D<sub>2</sub>. In fact, the only structural study of  $p$ -H<sub>2</sub> and  $o$ -D<sub>2</sub> at elevated pressures up to 2.5

GPa and low temperatures were made by Ishmaev *et al.* using the neutron diffraction method [10, 11]. It was found that the ratio  $c/a$  is practically constant and is slightly lower than the ideal hcp value ( $1.631 \pm 0.002$ ).

There were numerous structural studies of  $n$ -H<sub>2</sub> and  $n$ -D<sub>2</sub> [12–18] (see also reviews [19, 20]). Using new synchrotron x-ray diffraction techniques Mao *et al.* [14] and Hu *et al.* [15] found that in the case of  $n$ -H<sub>2</sub> the pressure dependence of  $c/a$  between 5 and 42 GPa is linear

$$c/a = 1.63 - 0.000441P, \quad (1)$$

where  $P$  is the pressure in GPa. Synchrotron single-crystal x-ray diffraction measurements of  $n$ -H<sub>2</sub> [21–23] and  $n$ -D<sub>2</sub> [21] up to megabar pressures at room temperature revealed that the  $c/a$  ratio decreases with increasing pressure near linearly up to 180 GPa. No isotope effect in the pressure dependence of the  $c/a$  ratio was found.

There have been many attempts to calculate the pressure behavior of the axial ratio using different theoretical approaches: Hartree-Fock [24, 25], local density approximation [26], path-integral Monte-Carlo [27], *ab initio* molecular dynamics [28]. In all proposed theoretical approaches the rotation-lattice coupling gives rise to positive  $\delta$  which is in contradiction with experiment.

In the present paper we develop a self-consistent approach based on the many-body semi-empirical intermolecular potential proposed originally in Ref. [29]. We are going to show that the pressure behavior of the  $c/a$ -ratio in solid  $p$ -H<sub>2</sub> and  $o$ -D<sub>2</sub> in phase I is determined mainly by the translational degrees of freedom and is comparable in magnitude with that for rare-gas solids. In the case of  $n$ -H<sub>2</sub> and  $n$ -D<sub>2</sub> we show that the behavior of the axial ratio found in Refs. [21–23] is due to the presence of the  $J$ -odd component in normal ortho-para mixtures of solid hydrogens [30].

The Hamiltonian of the problem can be written in the form [20, 29]

$$\mathcal{H} = \mathcal{H}_{\text{is}} + \mathcal{H}_{\text{rot}} + \mathcal{H}_{\text{int}}, \quad (2)$$

where  $\mathcal{H}_{\text{is}}$  is the contribution of the isotropic part of the intermolecular potential,  $\mathcal{H}_{\text{rot}}$  is the ro-

tational part of the Hamiltonian, and  $\mathcal{H}_{\text{int}}$  describes the lattice-rotation coupling.

The isotropic part of the ground-state energy  $E_{\text{is}}$  can be written as a sum of contributions from the isotropic part of the static two- and many-body energies  $E_{\text{is}}^{\text{pair}}$  and  $E_{\text{is}}^{\text{m.b.}}$ , and the zero-point vibrations  $E^{\text{zpv}}$ :

$$E_{\text{is}} = E_{\text{is}}^{\text{pair}} + E_{\text{is}}^{\text{m.b.}} + E^{\text{zpv}}. \quad (3)$$

In the mean field approximation (MFA), the Hamiltonian of the system of quantum linear rotors has the form [20, 29]:

$$\mathcal{H}_{\text{rot}} = \sum_f \mathbf{L}_f^2 - U_0 \sqrt{4\pi/5} \eta \sum_f Y_{20}(\vartheta_f) + \frac{1}{2} N U_0 \eta^2, \quad (4)$$

where  $\mathbf{L}_f$  is the angular momentum operator,  $Y_{LM}(\vartheta_f, \varphi_f)$  are spherical harmonics, and the angles  $\vartheta_f$  and  $\varphi_f$  specify the orientational axis of the molecule at the lattice site  $f$ . All the energy quantities are expressed in units of the rotational constant  $B_{\text{rot}}$ .

In distinction to the phases II and III, the phase I has no orientational structure which would originate from the coupling term in the anisotropic interaction between the hydrogen molecules. A certain degree of orientational order in the phase I as will be shown below originates from the crystal field interaction. The orientational order parameter is defined as

$$\eta = \sqrt{4\pi/5} \langle Y_{20}(\vartheta_f, \varphi_f) \rangle, \quad (5)$$

where  $\langle \dots \rangle$  means averaging with the Hamiltonian  $\mathcal{H}_{\text{rot}}$  (Eq. 4), and  $N$  is the number of sites.

The molecular field constant is defined by

$$U_0 = \sum_{ff'} \sum_{\alpha\beta\gamma\delta} V_{ff'}^{\alpha\beta\gamma\delta} Q_f^{\alpha\beta} Q_{f'}^{\gamma\delta}, \quad (6)$$

where  $V_{ff'}^{\alpha\beta\gamma\delta}$  is the interaction matrix defined by the parameters of the intermolecular potential,  $Q_f^{\alpha\beta} = \Omega_f^\alpha \Omega_f^\beta - \frac{1}{3} \delta_{\alpha\beta}$ ,  $\Omega$  is the unit vector specifying the equilibrium orientation of the molecule at the site  $f$ . There is a near linear correspondence between dimensionless pressure in units of  $U_0/B_{\text{rot}}$  and pressure in GPa. For the  $Pca2_1$  lattice we have the following approximate relations for rescaling the pressure:  $P$  in  $U_0/B_{\text{rot}}$  units

corresponds to  $0.5P$  in GPa for  $H_2$ ;  $0.75P$  for HD, and  $1.25$  for  $D_2$  [29]

The many-body hydrogen intermolecular potential used here is a sum of the pair SG potential [31] (discarding the  $R^{-9}$  term) and two three-body terms: the long-range Axilrod-Teller dispersive interaction and the short-range three-body exchange interaction in the Slater-Kirkwood form [32, 33]. It was successfully used for the description of the equation of state, the pressure dependence of the Raman-active  $E_{2g}$  mode [34], and the sound velocities in solid hydrogen under pressure [35]. The explicit form and parameters of the potential used in this work are given in Ref. 36. The contribution of the zero-point vibrations  $E^{zpv}$  was taken into account in the Einstein approximation.

In a non-rigid lattice there is a strong lattice-rotation coupling, which is due to the crystal field. The origin of this coupling can be explained in the following way. With increasing pressure the anisotropic interaction increases and admixtures of  $J \neq 0$  rotational states into the ground state wave function become more and more appreciable. With the nonzero admixture the molecules acquire anisotropy. The anisotropic molecules tend to be packed into a distorted lattice. The lattice distortion  $\delta$  is given by a competition of the anisotropic interactions (which favor strong distortion) and the isotropic interactions (which favor a near-ideal HCP lattice).

The lattice-rotation coupling is described by the the Hamiltonian

$$\mathcal{H}_{\text{int}} = -\varepsilon_{2c} \sqrt{4\pi/5} Y_{20}, \quad (7)$$

where  $\varepsilon_{2c}$  is the crystal-field parameter [37] which is linear with respect to  $\delta$ :

$$\varepsilon_{2c} = \tilde{B}\delta; \quad \tilde{B} = -\sqrt{6} \left( B + \frac{1}{2} R \frac{dB}{dR} \right), \quad (8)$$

where  $B(R)$  is the radial function of the single-molecular term in the anisotropic intermolecular potential [37]. Thus, the state of the lattice can be described by two coupled order parameters,  $\eta(V, T)$  and  $\delta(V, T)$ , which can be determined by the minimization of the free energy

with respect to these parameters. In the calculations we restrict ourselves to  $T = 0$  K case, so we will minimize the total ground-state energy  $E_0^{\text{tot}} = E_0^{\text{tr}} + E_0^{\text{rot}}$  (the superscripts "tot", "tr", and "rot" refer to the total ground-state energy, and translational, and rotational subsystems, respectively))

The translational part of the round-state energy  $E_0^{\text{tr}}$  does not depend on  $\eta$  and respective minimum conditions take the form:

$$\partial E_0^{\text{rot}} / \partial \eta = 0; \quad (9)$$

$$\partial (E_0^{\text{tr}} + E_0^{\text{rot}}) / \partial \delta = 0. \quad (10)$$

Thus, the complete minimization can be carried out in two stages, first, with the help of Eq. (9) we find  $\eta$  as a function of  $U_0$  and  $\delta$  and then by minimizing the total ground-state energy with respect to  $\delta$  (Eq. 10) we find  $\delta$  and  $\eta$  as a function of  $U_0$  (volume  $V$ ).

Using the successive approximation method we can find solutions of Eqs. (9), (10) in any necessary approximation [29, 36]. Up to the third order in the crystal-field parameter the orientational order parameter and orientational ground-state energy have the following form:

$$\eta = \kappa \frac{\varepsilon_{2c}}{B_{\text{rot}}} + \frac{15^2}{14} \kappa^3 \left( \frac{\varepsilon_{2c}}{B_{\text{rot}}} \right)^2. \quad (11)$$

$$\frac{E_0^{\text{rot}}}{B_{\text{rot}}} = -\frac{1}{2} \kappa \left( \frac{\varepsilon_{2c}}{B_{\text{rot}}} \right)^2 - \frac{75}{14} \kappa^3 \left( \frac{\varepsilon_{2c}}{B_{\text{rot}}} \right)^3. \quad (12)$$

where

$$\kappa = \frac{1}{15 - U_0/B_{\text{rot}}}. \quad (13)$$

The expansion parameter  $\varepsilon_{2c}$  (Eq. 8) is negative for all pressures, so the expansions Eqs. (11), (12) are oscillating and converge if the terms of the expansions are decreasing.

Due to the presence of a singular factor  $\kappa$  (Eq. 13) in the expansions Eqs. (11, 12), the validity of this analytical solution is limited by the condition  $U_0/B_{\text{rot}} < 15$ , which corresponds to pressure of  $\sim 30$  GPa for the case of  $p$ - $H_2$ , and

20 GPa and 12 GPa for HD and *o*-D<sub>2</sub>, respectively. To extend the solution into the higher pressure region a numerical approach should be used.

As can be seen from Eqs. (11), (12), at low pressures the rotational part of the ground-state energy contains no linear term in  $\delta$ . The same is also true at high pressures. The admixture of higher rotational states to the rotational wavefunction is proportional to the lattice distortion:

$$\Psi_0 = Y_{00} + c_2 \delta Y_{20} + \dots \quad (14)$$

The ground-state energy

$$E_0^{\text{rot}} = \langle \Psi_0 | \mathcal{H}_{\text{rot}} | \Psi_0 \rangle = 6c_2^2 \delta^2 - (U_0 \eta^2 / 2 + \epsilon_{2c} \eta). \quad (15)$$

Since  $\eta \sim \delta$  and  $\epsilon_{2c} \sim \delta$ ,  $E_0^{\text{rot}} \sim \delta^2$  at all pressures.

Let us consider the contribution of the translational degrees of freedom. Up to terms of the second order in  $\delta$  the translational part of the ground-state energy is

$$E_0^{\text{tr}} = E_0(0) + b_1^{\text{tr}} \delta + b_2^{\text{tr}} \delta^2, \quad (16)$$

where  $E_0$  is the ground-state energy of the ideal lattice and  $b_i^{\text{tr}}$  ( $i = 1, 2$ ) are the coefficients which depend on the parameters of the intermolecular potential and molar volume. The total ground-state energy is

$$E_0^{\text{tot}} = E_0(0) + b_1^{\text{tr}} \delta + b_2^{\text{tot}} \delta^2, \quad (17)$$

where  $b_2^{\text{tot}} = b_2^{\text{tr}} + b_2^{\text{rot}}$ . Minimizing  $E_0(\delta)$  over  $\delta$ , we obtain

$$\delta = -b_1 / (2 b_2^{\text{tot}}). \quad (18)$$

At small pressures the contribution of the rotational degrees of freedom to  $b_2$  as follows from Eq. (12) is  $b_2^{\text{rot}} = -\kappa (\epsilon_{2c}^2 / 2 B_{\text{rot}})$ . It is negative and increases in the absolute value with pressure. The total  $b_2^{\text{tot}}$  is a sum of the respective contributions

$$b_2^{\text{tot}} = b_2^{\text{tr}} + b_2^{\text{rot}}. \quad (19)$$

Figure 1 presents the lattice distortion parameter  $\delta$  and orientational order parameter  $\eta$  for *p*-H<sub>2</sub>, and *o*-D<sub>2</sub> as functions of molar volume. The calculations were performed for the molar

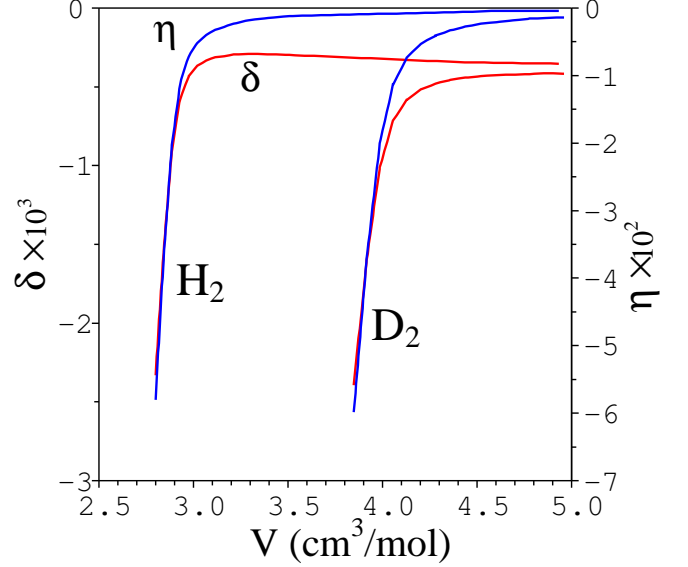


FIG. 1: Lattice distortion parameter  $\delta$  and orientational order parameter  $\eta$  in parahydrogen and orthodeuterium as functions of molar volume.

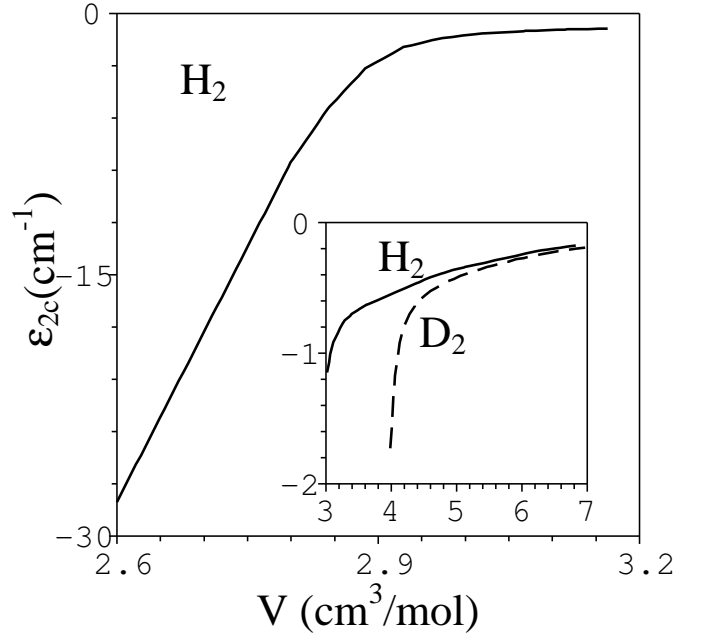


FIG. 2: Crystal field parameter  $\epsilon_{2c}$  in parahydrogen and orthodeuterium (inset) as functions of molar volume.

volumes  $V < 18 \text{ cm}^3/\text{mol}$  ( $P > 0.5 \text{ GPa}$ ) outside of the region where quantum crystal effects are decisive and extended up to the point of the I - II transition. In phase I both  $\eta$  and  $\delta$  are small and negative. The negative  $\delta$  means that the lat-

tice is slightly flattened compared with the ideal one; the negative  $\eta$  means that the molecules precess around the  $c$ -axis with the molecular axis inclined to the  $c$  axis by the angle slightly over  $\langle\vartheta_0\rangle = \cos^{-1} 1/\sqrt{3} \approx 54^\circ 44'$ . Upon increasing pressure,  $\eta$  decreases monotonically (the limiting value  $\eta = -1/2$  means that the molecules precess around the  $c$ -axis with the precession angle  $\vartheta = \pi/2$ ). At large molar volumes (18 cm<sup>3</sup>/mol) the deviation of the molecular ground state from the pure spherical one is very small. This deviation is characterized by the orientational order parameter  $\eta = -3.3 \cdot 10^{-4}$  for  $p$ -H<sub>2</sub> and  $\eta = -1 \cdot 10^{-5}$  for  $o$ -D<sub>2</sub>. The lattice is very close to the ideal one. While  $\eta$  decreases monotonically with rising pressure,  $\delta$  changes with pressure nonmonotonically (Figure 1). This non-monotonic behavior is connected with the mutual changes of the coefficients  $b_1^{\text{tr}}$ ,  $b_2^{\text{tr}}$ , and  $b_2^{\text{rot}}$  in Eq. (18) with pressure.

Significant changes are seen between  $V = 3.1$  ( $P = 80$  GPa) and  $2.93$  ( $P = 92.2$  GPa) cm<sup>3</sup>/mol for H<sub>2</sub> and between  $V = 4.05$  (37.45 GPa) and  $4.2$  (33.8 GPa) for D<sub>2</sub>, which corresponds to the I-II transition (experimentally, 110 GPa in  $p$ -H<sub>2</sub> [39], 28 GPa in  $o$ -D<sub>2</sub> [40]).

Knowing the pressure dependence of  $\delta$ , we were able to calculate the pressure dependence of the second order crystal field parameter  $\epsilon_{2c}$  (Fig. 8). As known [37], this parameter determines the splitting of the purely rotational band  $S_0(0)$  in  $p$ -H<sub>2</sub> and  $o$ -D<sub>2</sub> and splitting of the rotational levels of impurity  $J = 1$  molecules in  $J = 0$  solids. In the absence of direct experimental data some qualitative conclusions on the lattice distortion parameter of  $p$ -H<sub>2</sub> were obtained by Goncharov *et al.* [41]. The authors have measured low-frequency Raman spectra at low temperature for the pressure range up to the I - II phase transition and used these spectra to estimate the crystal-field parameter  $\epsilon_{2c}$ . Assuming that only the second-order crystal field is responsible for the splitting of the roton triplet band  $S_0(0)$  the authors obtained  $|\epsilon_{2c}| \sim 1$  cm<sup>-1</sup> and thus  $|\delta| \sim 10^{-3} - 10^{-4}$  in accord with theoretical data shown in Figs. (1, 2).

Characteristics of the rotational motion of the molecules in  $p$ -H<sub>2</sub> and  $o$ -D<sub>2</sub> could be com-

pared with the ones obtained using the technique which combines a density functional theory (DFT) with a path-integral molecular dynamics (PIMD) [38]. A direct comparison of the results involves difficulties because the authors used the definition of the orientational order parameter ( $\eta = [N^{-1} \sum_i^N \sqrt{4\pi/5} Y_{20}(\mathbf{\Omega}_i \cdot \mathbf{u}_i)]^2$  where  $\mathbf{\Omega}_i$  is a unit vector specifying the equilibrium orientation of the molecule at the site  $i$ , and  $\mathbf{u}_i$  is a site-specific unit vector which defines the orientational structure), which excludes negative values of the order parameter. Nonetheless, the pressure evolutions of the order parameters in the both approaches are similar.

Let us turn to the case of  $n$ -H<sub>2</sub>. For a single  $J = 1$  molecule in the lattice of  $J = 0$  molecules there is an additional contribution to the ground-state energy arising from the polarization of the surrounding  $J = 0$  molecules by the electric quadrupole field of the  $J = 1$  molecule. The polarization energy due to the interaction of the quadrupole moment of the  $J = 1$  molecule with the induced dipole moments of the surrounding nearest neighboring  $J = 0$  molecules is equal to [37]

$$\epsilon_1 = -18\alpha Q^2 V^{-8/3}, \quad (20)$$

where  $\alpha$  is the polarizability of the  $J = 0$  molecules and  $Q$  is the quadrupole moment of the  $J = 1$  molecule.

If the crystal shows a homogeneous deviation from the ideal hcp structure specified by the lattice distortion parameter  $\delta$ , the polarization energy contains a crystal-field term [37]

$$V_c = \epsilon_{2c} \sqrt{\frac{4\pi}{5}} Y_{20}(\vec{\Omega}), \quad (21)$$

where  $\vec{\Omega}$  specifies the orientation of the  $J = 1$  molecule with

$$\epsilon_{2c} = -\frac{24}{7} \epsilon_1 \delta. \quad (22)$$

The triplet  $J = 1$  level is splitted in the crystal field  $V_c$ ; the splitting is given by

$$\Delta_c = E(\pm) - E(0) = \frac{3}{5} |\epsilon_{2c}|, \quad (23)$$

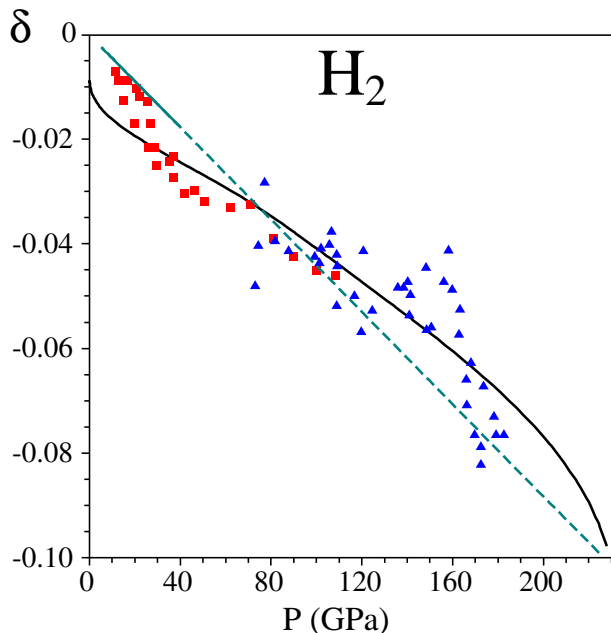


FIG. 3: Lattice distortion parameter in normal ortho-para mixture of solid hydrogens. Theory: solid line - this work; experiment: red squares - data from Ref. [21], blue triangles - data from Ref. [23], green straight line: Eq. (1) (solid section [14, 15], dashed section - extrapolation to high pressures.)

where  $E(M)$  is the energy of the state  $J = 1$ ,  $J_z = M$  with  $z$  direction parallel to the  $c$  axis of the crystal. The positive sign of  $\Delta_c$  implies that the state  $J_z = 0$  is the ground state of the triplet. Due to this splitting the ground-state energy is brought down by  $2|\varepsilon_{2c}|/5$ . The gain in the anisotropic energy due to the polarization effect in the  $J = 0/J = 1$  mixture is linear in  $\delta$ , contrary to the contribution quadratic in  $\delta$  in  $J$ -even solids. At the same time, this distortion introduces an additional positive contribution to the ground-state energy from the isotropic part of the intermolecular interaction. This contribution is quadratic in the lattice distortion parameter  $\delta$  [36]. The loss in the isotropic part and the gain in the anisotropic part of the ground-state energy determines the lattice distortion parameter at the given molar volume. One cannot obtain a reliable value of  $\delta$  from Eqs. (20) - (23) because there are other contributions to the splitting  $\Delta_c$  not included in Eq. (23) [37]. Moreover, the lattice of  $n$ - $H_2$  is a disordered mixture of ortho and para molecules. To calculate

the polarization energy in such lattice we used a mean-field model of ortho-para mixture assuming that each site of the lattice is occupied by a superposition of even- $J$  and odd- $J$  molecule and the crystal field splitting occurs for every ortho-component of such molecule. Assuming that the volume dependence of the polarization energy has the same form as in Eq. (20) we included into the ground-state energy the term

$$E_{\text{pol}} = A(V_0/V)^{8/3}\delta, \quad (24)$$

where  $A$  is an adjusting parameter of the theory. Comparing with the experimental data on the pressure dependence of the lattice distortion parameter from Refs. [21, 23] we obtain a good fit for  $A = 5.1$  K. The resulting pressure dependence of the lattice distortion parameter is presented in Fig. 3. Comparing this result with the one for  $p$ - $H_2$  (Fig. 1), we see that the introduction of the  $J = 1$  molecules increases the hcp lattice distortion by two orders of magnitude.

In conclusion, we developed the lattice-dynamics theory of the lattice distortion in  $p$ -hydrogen,  $o$ -deuterium, and  $n$ -hydrogen in hexagonal closed-packed lattice under pressure. It is shown that the lattice distortion in  $p$ - $H_2$  and  $o$ - $D_2$  is negative and very small (of the order of  $10^{-3}$ ) and their lattices are very close to the ideal one. In this aspect the  $J$ -even modifications of hydrogens are very similar to solid helium. The main contributions to the lattice distortion comes from translational degrees of freedom, although there is a nonzero contribution from rotational degrees of freedom as well. The negative sign of the lattice distortion parameter means that the lattice is slightly flattened. The orientational order parameter was calculated and shown to be small and negative. The molecules rotate around the  $c$ -axis with the inclination angle  $\vartheta \approx 55^\circ$ .

A mean-field model of the ortho-para mixture of solid hydrogen was developed to calculate the polarization energy connected with the impurity ortho molecules. It is shown that there is a considerable gain in the ground-state energy of the mixture due to the polarization energy, which makes the lattice distortion advantageous. The corresponding loss in the energy of the isotropic

interaction determines the resulting value of the lattice distortion parameter. Obtained pressure dependence of the  $c/a$  ratio is in an excellent agreement with the experiment in the whole pressure range.

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\* Electronic address: yuri.afreiman@gmail.com

- [1] R. Howard, Phys. Lett **32A**, 37 (1970).
- [2] P. Schwerdtfeger, N. Gaston, R. P. Krawczyk, R. Tonner, and G. E. Moyano, Phys. Rev. B **73**, 064112 (2006).
- [3] F. H. Stillinger, J. Chem. Phys. **115**, 5208 (2001).
- [4] Yu. A. Freiman, S. M. Tretyak, A. Grechnev, A. F. Goncharov, J. S. Tse, D. Errandonea, H.-k. Mao, and R. J. Hemley, Phys. Rev. B **80**, 094112 (2009).
- [5] A. Grechnev, S. M. Tretyak, and Yu. A. Freiman, Low Temp. Phys. **36**, 333 (2010) [*Fizika Nizkikh Temperatur* **36**, 423 (2010)].
- [6] Yu. A. Freiman, S. M. Tretyak, F. Jezowski, and R. J. Hemley, J. Low. Temp. Phys. **126**, 703 (2002).
- [7] Neil W. Ashcroft and N. David Mermin, *Solid State Physics* (Holt, Rinehalt, and Winston, New York, 1976).
- [8] W. H. Keesom, J. de Smedt, and H. H. Moon, *Leiden Commun.* **19**, Suppl. No. 69, No. 209d (1929/1930).
- [9] I. N. Krupskii, A. I. Prokhvatilov, and G. N. Shcherbakov, Sov. J. Low Temp. Phys. **9**, 42 (1983); **10**, 1 (1984).
- [10] S. N. Ishmaev, I. P. Sadikov, A. A. Chernyshov, B. A. Vindryaevskii, V. A. Sukhoparov, A. Telepnev, and G. V. Kobelev, Sov. Phys. JETP **57**, 228 (1983).
- [11] S. N. Ishmaev, I. P. Sadikov, A. A. Chernyshov, B. A. Vindryaevskii, V. A. Sukhoparov, A. Telepnev, G. V. Kobelev, and R. A. Sadikov, Sov. Phys. JETP **62**, 721 (1985).
- [12] R.M. Hazen, H. K. Mao, L. W. Finger, and R. J. Hemley, Phys. Rev. B **36** (1987) 3944.
- [13] V. P. Glazkov, S. P. Besedin, I. N. Goncharenko, A. V. Irodova, I. N. Makarenko, V. A. Somenkov, S. M. Stishov, and S. Sh. Shil'shtein, JETP Lett. **47**, 763 (1988).
- [14] H. K. Mao, A. P. Jephcoat, R. J. Hemley, L. W. Finger, C. S. Zha, R. M. Hazen, and D. E. Cox, Science **239** 1131 (1988).
- [15] J. Hu, H.K. Mao, J. F. Shu, and R. J. Hemley, unpublsh.
- [16] R.J. Hemley, H.K. Mao, L.W. Finger, A.P. Jephcoat, R.M. Hazen, and C.S. Zha, Phys. Rev. B **42** 6458, (1990).
- [17] S. P. Besedin, I. N. Makarenko, S. M. Stishov, V. P. Glazkov, S. I. N. Goncharenko, A. V. Irodova, V. A. Somenkov, and S. Sh. Shil'shtein, High-Pressure research **4**, 447 (1990).
- [18] S. P. Besedin, I. N. Makarenko, S. M. Stishov, V. P. Glazkov, S. I. N. Goncharenko, A. V. Irodova, V. A. Somenkov, and S. Sh. Shil'shtein, in *Molecular Systems Under High Pressure*, edited by R. Pucci and G. Piccitto (Elsevier, North-Holland, 1991)
- [19] H.-k. Mao and Russell J. Hemley, Rev. Mod. Phys. **66**, 671 (1994).
- [20] *Physics of Cryocrystals*, eds. V.G. Manzhelii and Yu.A. Freiman (AIP Press, New York, 1997).
- [21] P. Loubeyre, R. LeToullec, D. Hausermann, M. Hanfland, R. J. Hemley, H. K. Mao, and L. W. Finger, Nature **383**, 702 (1996).
- [22] H. Kawamura, Y. Akahama, S. Umemoto, K. Takemura, Y. Ohishi, and O. Shimomura, J. Phys.: Condens. Matter **14**, 10407 (2002).
- [23] Y. Akahama, M. Nishimura, H. Kawamura, N. Hirao, Y. Ohishi, and K. Takemura, Phys. Rev. B **82**, 060101(R) (2010).
- [24] S. I. Anisimov and Yu. V. Petrov, JETP Lett. **26**, 446 (1977)
- [25] S. Raynor, J. Chem. Phys. **87**, 2795 (1987).
- [26] T. W. Barbee, A. Garcia, and M. L. Cohen, Phys. Rev. Lett. **62**, 1150 (1989).
- [27] T. Cui, E. Cheng, B.J. Alder, and K.B. Whaley, Phys. Rev. B **55** (1997) 12 253.
- [28] J. Kohanoff, S. Scandolo, G. L. Chiarotti, and E. Tosatti, Phys. Rev. Lett. **78**, 2783 (1997).
- [29] Yu.A. Freiman, S. Tretyak, and A. Jezowski, and R. J. Hemley, J. Low Temp. Phys. **122** (2001) 537.
- [30] J. Igarashi, J. Phys. Soc. Jap. **59**, 2811 (1990)
- [31] I. F. Silvera and V. V. Goldman, J. Chem. Phys. **69**, 4209 (1978).
- [32] P. Loubeyre, Phys. Rev. Lett. **58**, 1857 (1987); Phys. Rev. B **37**, 5432 (1988).
- [33] Yu. A. Freiman, A. F. Goncharov, S. M. Tretyak, A. Grechnev, J. S. Tse, D. Errandonea, H.-k. Mao, and R. J. Hemley, Phys. Rev. B **78**, 014301 (2008).
- [34] Yu.A. Freiman, Alexei Grechnev, S. M. Tretyak, Alexander Goncharov, and Russell J. Hemley, Phys. Rev. B **86**, 014111 (2012).
- [35] Yu. A. Freiman, Alexei Grechnev, S. M. Tretyak, A. F. Goncharov, C. S. Zha and Russell J. Hemley, Phys. Rev. B **88**, 214501 (2013).
- [36] Yu. A. Freiman, S. M. Tretyak, Alexander F. Goncharov, Ho-kwang Mao and Russell J. Hemley, Low Temp. Phys. **37**, 1038 (2011).
- [37] J. Van Kranendonk: *Solid Hydrogen* (Plenum, New York 1983).
- [38] G. Geneste, M. Torrwent, F. Bottin, and P. Loubeyre, Phys. Rev. Lett. **109**, 155303 (2014)
- [39] H. E. Lorenzana, I. F. Silvera, and K. A. Goettel, Phys. Rev. Lett. **64**, 1939 (1990).
- [40] I. F. Silvera, R. J. Wijngaarden, Phys. Rev. Lett. **47**, 39 (1981)
- [41] A. F. Goncharov, M. A. Strzhemechny, H. K. Mao, and R. J. Hemley, Phys. Rev. B **63**, 064304 (2001).